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## (54) SUBLIMATION GROWTH OF SILICON CARBIDE SINGLE CRYSTALS

SUBLIMATIONSANWACHSEN VON SILIZIUMKARBIDEINKRISTALLEN

CROISSANCE DE MONOCRISTAUX DE CARBURE DE SILICIUM PAR SUBLIMATION

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**Description**

The present invention is a method for controlling the sublimation growth of silicon carbide to produce high quality single crystals.

5       Silicon carbide is a perennial candidate for use as a semiconductor material. Silicon carbide has a wide bandgap (2.2 electron volts in the beta polytype, 2.8 in the 6H alpha), a high thermal coefficient, a low dielectric constant, and is stable at temperatures far higher than those at which other semiconductor materials such as silicon remain stable. These characteristics give silicon carbide excellent semiconducting properties, and electronic devices made from silicon carbide can be expected to perform at higher temperatures, and at higher radiation densities, than devices made 10 from the presently most commonly used semiconductor materials such as silicon. Silicon carbide also has a high saturated electron drift velocity which raises the potential for devices which will perform at high speeds, at high power levels, and its high thermal conductivity permits high density device integration.

15       As is known to those familiar with solid state physics and the behavior of semiconductors, in order to be useful as a material from which useful electrical devices can be manufactured, the basic semiconductor material must have certain characteristics. In many applications, a single crystal is required, with very low levels of defects in the crystal lattice, along with very low levels of unwanted impurities. Even in a pure material, a defective lattice structure can prevent the material from being useful for electrical devices, and the impurities in any such crystal are preferably carefully controlled to give the desired electrical characteristics. If the impurities cannot be controlled, the material is generally unsatisfactory for use in electrical devices.

20       Accordingly, the availability of an appropriate crystal sample of silicon carbide is a fundamental requirement for the successful manufacture of devices from silicon carbide which would have the desirable properties described above. Such a sample should be of a single desired crystal polytype (silicon carbide can form in at least 150 types of crystal lattices), must be of a sufficiently regular crystal structure of the desired polytype, and must be either substantially free of impurities, or must contain only those impurities selectively added to give the silicon carbide any desired n or p character.

25       Accordingly, and because the physical characteristics and potential uses for such silicon carbide have been recognized for some time, a number of researchers have suggested a number of techniques for forming crystalline silicon carbide.

30       These techniques generally fall into two broad categories, although it will be understood that some techniques are not necessarily so easily classified. The first technique is known as chemical vapor deposition (CVD) in which reactants gases are introduced into some sort of system within which they form silicon carbide crystals upon an appropriate substrate. Novel and commercially significant improvements in such CVD techniques are discussed in currently co-pending United States applications which are assigned to us "Growth of Beta-SiC Thin Films and Semiconductor Devices Fabricated Thereon," Serial No. 113,921, filed October 26, 1987; and "Homoepitaxial Growth of Alpha-SiC Thin 35 Films and Semiconductor Devices Fabricated Thereon," Serial No. 113,573, filed October 26, 1987.

40       The other main technique for growing silicon carbide crystals is generally referred to as the sublimation technique. As the designation sublimation implies and describes, sublimation techniques generally use some type of solid silicon carbide material, other than a desired single crystal of a particular polytype, as a starting material, and then heat the starting material until solid silicon carbide sublimes. The vaporized material is then encouraged to condense, with the condensation intended to produce the desired crystals.

45       As is known to those familiar with the physical chemistry of solids, liquids and gases, crystal growth is encouraged when the seed or surface upon which a crystal is being formed is at a somewhat lower temperature than the fluid, either gas or liquid, which carries the molecules or atoms to be condensed.

50       One technique for producing solid silicon carbide when crystal-type impurity is of little consideration is the Acheson furnace process, which is typically used to produce silicon carbide for abrasive purposes. One of the first sublimation techniques of any practical usefulness for producing better crystals, however, was developed in the 1950's by J. A. Lely, one technique of whom is described in U.S. Patent No. 2,854,364. From a general standpoint, Lely's technique lines the interior of a carbon vessel with a silicon carbide source material. By heating the vessel to temperatures at which silicon carbide sublimes, and then allowing it to condense, recrystallized silicon carbide is encouraged to redeposit itself along the lining of the vessel. Although the Lely process can generally improve upon the quality of the source material, it has to date failed to produce on a consistent or repeatable basis, single crystals of silicon carbide suitable for electrical devices.

55       Hergenrother, U.S. Patent No. 3,228,756, discusses another sublimation growth technique which utilizes a seed crystal of silicon carbide upon which other silicon carbide can condense to form the crystal growth. Hergenrother suggests that in order to promote proper growth, the seed crystal must be heated to an appropriate temperature, generally over 2000° centigrade, in such a manner that the time period during which the seed crystal is at temperatures between 1800°C and 2000°C is minimized.

Ozarow, U.S. Patent No. 3,236,780, discusses another unseeded sublimation technique which utilizes a lining of

silicon carbide within a carbon vessel, and which attempts to establish a radial temperature gradient between the silicon carbide-lined inner portion of the vessel and the outer portion of the vessel.

Knippenberg, U.S. Patents Nos. 3,615,930 and 3,962,406, discuss alternative attempts at growing silicon carbide in a desired fashion. The '930 patent discusses a method of growing p-n junctions in silicon carbide as a crystal grows by sublimation. According to the discussion in this patent, silicon carbide is heated in an enclosed space in the presence of an inert gas containing a donor-type dopant atom, following which the dopant material is evacuated from the vessel and the vessel is reheated in the presence of an acceptor dopant. This technique is intended to result in adjacent crystal portions having opposite conductivity types and forming a p-n junction.

In the '406 patent, Knippenberg discusses a three-step process for forming silicon carbide in which a silicon dioxide core is packed entirely within a surrounding mass of either granular silicon carbide or materials which will form silicon carbide when heated. The system is heated to a temperature at which a silicon carbide shell forms around the silicon dioxide core, and then further heated to vaporize the silicon dioxide from within the silicon carbide shell. Finally, the system is heated even further to encourage additional silicon carbide to continue to grow within the silicon carbide shell.

Vodadkof, U.S. Patent No. 4,147,572, discusses a geometry-oriented sublimation technique in which solid silicon carbide source material and seed crystals are arranged in parallel close proximity relationship to one another.

Addamiano, U.S. Patent No. 4,556,436, discusses a Lely-type furnace system for forming thin films of beta silicon carbide on alpha silicon carbide which is characterized by a rapid cooling from sublimation temperatures of between 2300° centigrade and 2700° centigrade to another temperature of less than 1800° centigrade.

Addamiano notes that large single crystals of cubic (beta) silicon carbide are simply not available and that growth of silicon carbide on other materials such as silicon or diamond is rather difficult.

Hsu, U.S. Patent No. 4,664,944, discusses a fluidized bed technique for forming silicon carbide crystals which resembles a chemical vapor deposition technique in its use of non-silicon carbide reactants, but which includes silicon carbide particles in the fluidized bed, thus somewhat resembling a sublimation technique.

Some of the more important work in the silicon carbide sublimation techniques, however, is described in materials other than United States patents. For example, German (Federal Republic) Patent No. 3,230,727 to Siemens Corporation discusses a silicon carbide sublimation technique in which the emphasis of the discussion is the minimization of the thermal gradient between silicon carbide seed crystal and silicon carbide source material. This patent suggests limiting the thermal gradient to no more than 20° centigrade per centimeter of distance between source and seed in the reaction vessel. This patent also suggests that the overall vapor pressure in the sublimation system be kept in the range of between 1 and 5 millibar and preferably around 1.5 to 2.5 millibar.

This German technique, however, can be considered to be a refinement of techniques thoroughly studied in the Soviet Union, particularly by Y.M. Tairov: see e.g. General Principles of Growing Large-Size Single Crystals of Various Silicon Carbide Polytypes, J. Crystal Growth, 52 (1981) 146-150, and Progress in Controlling the Growth of Polytypic Crystals, from Crystallization and Characterization of Polytype Structures, edited by P. Krishna, Pergamon Press, London, 1983, p. 111. Tairov points out the disadvantages of the Lely method, particularly the high temperatures required for crystal growth (2600°-2700°C) and the lack of control over the resulting crystal polytype. As discussed with reference to some of the other investigators in patent literature, Tairov suggests use of a seed as a method of improving the Lely process. In particular, Tairov suggests controlling the polytype growth of the silicon carbide crystal by selecting seed crystals of the desired polytype or by growing the recondensed crystals on silicon carbide faces worked at an angle to the 0001 face of the hexagonal lattice. Tairov suggests axial temperature gradients for growth of between approximately 30° and 40° centigrade per centimeter.

In other studies, Tairov investigated the effects of adjusting various parameters on the resulting growth of silicon carbide, while noting that particular conclusions are difficult to draw. Tairov studied the process temperatures and concluded that growth process temperature was of relatively smaller importance than had been considered by investigators such as Knippenberg. Tairov likewise was unable to draw a conclusion as to the effect of growth rate on the formation of particular polytypic crystals, concluding only that an increase in crystal growth rate statistically corresponds to an increase in the percentage of disordered structured crystals. Tairov was similarly unable to draw any conclusions between vapor phase stoichiometry and crystal growth, but pointed out that certain impurities will favor the growth of particular silicon carbide polytype crystals. For example, high nitrogen concentrations favor cubic polytype silicon carbide crystals, aluminum and some other materials favor the growth of hexagonal 4H polytype, and oxygen contributes to the 2H polytype. Tairov concluded that no understanding of the mechanisms leading to these effects had yet been demonstrated.

In Tairov's experiments, he also attempted using silicon carbide single crystals of particular polytypes as the vapor source material and suggested that using such single crystals of particular polytypes as vapor sources could result in particular polytypes of crystal growth. Of course, it will be understood that although the use of single crystals as source materials is theoretically interesting, a more practical goal, particularly from a commercial standpoint, is the production of single crystals from more common sources of silicon carbide other than single crystals.

Finally, Tairov concluded that the treatment of the substrate surface upon which sublimation growth was directed

could affect the growth of the resulting crystals. Nevertheless, the wide variety of resulting data led Tairov to conclude that additional unidentified factors were affecting the growth he observed in silicon carbide crystals, and these unknown factors prevented him from reaching a fundamental understanding of the mechanisms of crystal growth.

5 Therefore, in spite of the long recognized characteristics of silicon carbide, and the recognition that silicon carbide could provide an outstanding, if not revolutionary, semiconductor material and resulting devices, and in spite of the thorough investigations carried out by a number of researchers including those mentioned herein, prior to the present invention there existed no suitable technique for repeatedly and consistently growing large single crystals of desired selected polytypes of silicon carbide.

10 Accordingly, it is an object of the present invention to provide a method for the controlled, repeatable growth of large single crystals of silicon carbide of desired polytypes.

According to one aspect of the present invention, there is provided a method of reproducibly controlling the growth of large single crystals of a single polytype of silicon carbide independent of the use of impurities as a primary mechanism for controlling polytype growth, as defined in claim 1.

15 In one embodiment of the present invention, large single crystals of silicon carbide may be grown by controlling the polytype of the source material. Additionally or alternatively, source materials may be selected having a particular surface area and/or predetermined particle size distributions. Source materials other than single crystals of silicon carbide are employed.

20 In another method of growing such silicon carbide single crystals using sublimation techniques, the thermal gradient between the source materials and the seed is continuously adjusted to maintain the most favourable conditions possible for continued growth of silicon carbide crystals over longer time periods and into larger crystals than have previously ever been accomplished.

Reference will now be made to the accompanying drawings, wherein:-

25 Figure 1 is a cross-sectional diagram of a sublimation crucible used in accordance with the method of the present invention:

Figure 2 is an enlarged view of the seed crystal holder of the crucible of Figure 1,

Figure 3 is a cross-sectional diagram of a sublimation furnace used in accordance with the method of the present invention:

30 Figure 4 is a diagram of a sublimation system illustrating a screw type mechanism for continuously introducing silicon carbide source powder into a system; and

Figure 5 is a diagram of a sublimation system illustrating independent heating elements used in accordance with the method of the present invention.

35 Figure 1 illustrates a cross-sectional view of a sublimation crucible used in accordance with the method of the present invention. The crucible is broadly designated at 10 and is typically formed of graphite. Crucible 10 is generally cylindrical in shape and includes a porous graphite liner 11, a lid 12, and a seed holder 13, an enlarged view of which is illustrated in Figure 2. The remainder of the crucible is defined by the walls 14 and the floor 15. As further illustrated in Figure 1, the porous graphite liner 11 is formed in such a manner as to provide an annular chamber 16 between lower portions of the porous graphite liner 11, the crucible walls 14 and the crucible lid 12. A central sublimation chamber is illustrated at 20..

40 In all of the apparatus described herein, the crucibles described are preferably formed of graphite and most preferably of a graphite which has approximately the same coefficient of thermal expansion as silicon carbide. Such materials are commercially available. The relative similarities of thermal coefficients of expansion are a particular requirement for materials which are being heated to the extremely high temperatures described herein and at which these processes take place. In this manner, the crucible can be prevented from cracking during the sublimation process and the lifetime of the crucible will generally be increased.

45 Furthermore, as is recognized by those familiar with attempts at growing silicon carbide crystals, the presence of graphite in the system encourages the growth of silicon carbide by providing an equilibrium source of carbon atoms as the sublimation process takes place and by dampening variations in the flux.

50 Furthermore, graphite is one of the few economically viable materials which can both withstand the high temperatures of these processes and avoid introducing undesired impurities into the vapor flux.

55 The seed holder 13 is illustrated in more detail in Figure 2. A seed crystal 17 rests on upper portions of the seed holder 13 which extend into the chamber 20. A graphite washer 21 is positioned between the lower portions of the seed holder 13 and the floor of the crucible 15. Figure 2 also shows an optical opening 22, which in preferred embodiments of the invention provides optical access to the seed so that the temperature of the seed can be monitored with an optical pyrometer.

A sublimation crucible such as illustrated in Figure 1 is typically used in conjunction with a sublimation furnace broadly designated at 23 in Figure 3, in which the crucible is again designated 10. Furnace 23 is generally cylindrical

in shape and includes a cylindrical heating element 24, opposite portions of which are shown in the drawing. Furnace 23 is also surrounded by carbon fiber insulation 25 and includes optical ports 26, 27, and 28 through which optical pyrometers can measure the temperature of portions of the interior of the furnace. A power feed-through is generally designated at 30, and the outer housing of the furnace at 31.

5 In a first embodiment of the invention, a single seed crystal of silicon carbide having a desired polytype, and silicon carbide source powder, are introduced into a system such as the sublimation crucible and furnace illustrated in Figures 1-3. Where the crucible is of the type illustrated in Figure 1, the silicon carbide source powder is positioned in the annular chamber 16. In this first embodiment of the invention, it has been discovered that by utilizing silicon carbide source powder, substantially all of which has a constant polytype composition, the production of a desired crystal 10 growth upon the seed crystal can be greatly improved.

15 Although applicant does not wish to be bound by any particular theory, it is known that different polytypes of silicon carbide have different evaporation activation energies. Specifically, for cubic (3C) silicon carbide the evaporation activation energy is 452 kilojoules (kJ) per mole (108 kilocalories (kcal) per mole); for hexagonal 4H silicon carbide, 602 kJ/mole (144 kcal/mole); and for hexagonal 6H silicon carbide, 498 kJ/mole (119 kcal/mole). These differences are important, because when silicon carbide sublimes, it forms three basic vaporized materials: Si, Si<sub>2</sub>C, and SiC<sub>2</sub>. Depending upon the polytype of the source powder, the amount or "flux" of each of the species which is generated will differ. In a corresponding manner, the amount of each of the species in the overall vapor flux will tend to influence the type of polytypes which will grow when the species recondense.

20 As used herein, the term "flux" refers to the amount of matter or energy passing through a designated plane of a given area during a given period of time. Accordingly, when used to describe the flow of vaporized species, flux can be measured and designated in units of matter, area and time such as grams per square centimeter per second (g/cm<sup>2</sup>/sec).

25 As used herein, the term "constant polytype composition" refers to a source powder or powders which are made up of a constant proportion of certain polytypes, including single polytypes. For example, a source powder which was formed substantially entirely of 6H alpha silicon carbide would exhibit a constant polytype composition, as would source powder that was 50 percent alpha polytype and 50 percent beta polytype. In other words, the composition--whether homogeneous or heterogeneous with respect to polytypes--must be controlled so as to remain the same throughout the sublimation process.

30 Stated more directly, if the source powder is selected and controlled so that substantially it has a constant polytype composition, the relative amounts or ratios of Si, Si<sub>2</sub>C, and SiC<sub>2</sub> which are generated will remain constant and the other parameters of the process can be appropriately controlled to result in the desired single crystal growth upon the seed crystal. Alternatively, if the source powder is a variable mixture of various proportions of polytypes of silicon carbide, the relative amounts (ratios) of Si, Si<sub>2</sub>C, and SiC<sub>2</sub> which are generated will continually vary and correspondingly 35 continually encourage alternative polytypes to simultaneously grow upon the seed crystal. This results in growth upon the seed crystal of a number of crystals of different polytypes, an undesirable result.

Once the silicon carbide source powder and the seed crystal are introduced, the temperature of the silicon carbide source powder is raised to a temperature sufficient for silicon carbide to sublime from the source powder, typically a temperature on the order of 2300°C. While the temperature of the source powder is being raised, the temperature of the growth surface of the seed crystal is likewise raised to a temperature approaching the temperature of the source powder, but lower than the temperature of the source powder and lower than that at which silicon carbide will sublime. Typically, the growth surface of the seed crystal is heated to about 2200°C. By maintaining the silicon carbide source powder and the growth surface of the silicon carbide seed crystal at their respective temperatures for a sufficient time, macroscopic growth of monocrystalline silicon carbide of a desired polytype will form upon the seed crystal.

40 It will be understood by those familiar with phase changes that sublimation and condensation are equilibrium processes, and are affected by the vapor pressure of a system as well as absolute and relative temperatures. Accordingly, it will be further understood that in the processes and systems described herein, the vapor pressures are suitably controlled in a manner which permits these processes to proceed and be controlled and adjusted based upon the temperature and thermal gradient considerations described herein.

45 Further to the present invention, it has been discovered that in addition to maintaining a constant polytype composition, in order to form appropriate single crystals by the sublimation method, selecting silicon carbide source powder of a consistent particle size distribution similarly enhances the technique. In a manner similar to that set forth earlier, the control of particle size in a consistent manner results in a consistent flux profile of the species which evolve from the silicon carbide source powder, with a corresponding consistency in the sublimation growth of silicon carbide upon the seed crystal. In one embodiment, a powder having the following particle size distribution enhanced the process, 50 the distribution being defined by the weight percentage of a sample which will pass through a designated Tyler mesh screen:

Tyler Mesh Screen	Weight Percent Passed
20-40	43%
40-60	19%
60-100	17%
Over 100	21%

5 Additionally, for a given powder morphology, the exposed surface area of the source powder is proportional to the particle size. A consistency in exposed surface area in turn enhances the overall consistency of the vapor flux, so that controlling the size distribution in this manner enhances the consistency of the flux profile.

10 As in the other embodiments discussed, the silicon carbide source powder and the growth face of the seed crystal are both heated to respective different temperatures, with the growth face of the seed crystal being somewhat cooler than the source powder so as to encourage condensation of the sublimed species from the source powder onto the seed crystal.

15 In another embodiment of the invention, it has been discovered that controlling the thermal gradient between the growth surface of the seed crystal and the source powder results in appropriate control and growth of large single crystals having a desired polytype. In this respect, the thermal gradient can be controlled in a number of ways. For example, under certain circumstances the thermal gradient is controlled so as to remain constant between the growth surface of the seed crystal while under other circumstances, controllably changing the thermal gradient between the source powder and the growth surface of the seed crystal is preferred.

20 As is known to those familiar with various sublimation techniques, a thermal gradient is often introduced by physically separating the source powder from the seed crystal while they are being maintained at their respective different temperatures. The resulting thermal gradient is thus a function of geometric separation between the source powder and the growth surface of the seed crystal: e.g. 20°C per centimeter and the like. Thus, if the source powder is initially maintained at a temperature of, for example, 2300°C, and the growth surface of the seed crystal is maintained at a temperature of, for example, 2200°C and a distance of 10 centimeters is initially maintained between the source powder and the seed crystal, a thermal gradient of 100°C divided by 10 centimeters, i.e. 10°C per centimeter, will be established.

25 In one embodiment of thermal gradient control, the invention comprises introducing the seed single crystal of silicon carbide of a desired polytype and a silicon carbide source powder into a sublimation system. The temperature of the silicon carbide source powder is raised to a temperature sufficient for the silicon carbide to sublime and a thermal gradient is introduced between the growth surface of the seed crystal and the source powder by elevating the temperature of the seed crystal to a temperature approaching the temperature of the source powder, but lower than the temperature of the source powder and lower than that at which silicon carbide will sublime, under the vapor pressure conditions of the system. As the crystal grows and the source powder generally nearest the top of the crucible is used up, the thermal gradient between the growth surface of the seed crystal and the source powder is increased to thereby continuously encourage further crystal growth beyond that which would be obtained by maintaining a constant thermal gradient.

30 During the sublimation growth process, gas species which contain silicon carbide evolve near the hotter top of the crucible and are transported via the thermal gradient to the seed at its respective lower temperature in the cooler lower portion of the crucible. The source material, however, is also in the thermal gradient and sublimation of the source material tends to occur at a much faster rate in the upper portion of the source material than in the lower portion. As a result if the temperature gradient remains constant, a rapid decrease in flux with time occurs as the upper source material is depleted. In a similar manner, as the crystal grows, its growth surface increases in temperature as a result of its change in position with respect to the thermal gradient. This causes a decrease in the sticking coefficient as a function of time and likewise reduces the growth rate.

35 According to the present invention, however, it has been discovered that if the thermal gradient is continually increased as the source powder is depleted and as the seed crystal grows, the absolute temperature difference between the source and seed can be maintained at an amount which continues to be most favorable for crystal growth.

40 In one embodiment of the invention, control of the thermal gradient comprises the step of increasing the thermal gradient between the growth surface of the seed crystal and the source powder, and the same is accomplished by increasing the temperature of the source powder while maintaining the temperature of the growth surface of the seed crystal at the initial lower temperature than the source powder.

45 In another embodiment, the invention comprises maintaining a constant thermal gradient as measured between the growth surface of the seed crystal and the source powder as the crystal grows and as the source powder is used up. It will be understood that the temperature of the growth surface is the most critical temperature with respect to the crystal as the growth surface is the surface at which thermodynamic conditions will either favor or disfavor continued

desired growth of the crystal.

Accordingly, in another embodiment of the invention, the step of maintaining a fixed thermal gradient between the growth surface of the seed crystal and the source powder comprises providing relative movement between the growth surface of the seed crystal and the source powder as the seed crystal grows while maintaining the source powder and the growth face of the seed crystal at their respective different, but constant, temperatures.

In another embodiment, the step of maintaining a fixed thermal gradient between the growth surface of the seed crystal and the source powder comprises maintaining a fixed geometric distance between the growth surface of the seed crystal and the source powder as the crystal grows.

In yet another embodiment, the method of maintaining a constant thermal gradient between the growth surface of the seed crystal and the source powder can comprise independently controlling the source powder and seed crystal temperatures by separately monitoring the temperature of the source powder and the temperature of the seed crystal and separately adjusting the temperature of the source powder and the temperature of the seed crystal to maintain the desired thermal gradient.

In another embodiment of the invention, it has been discovered that growth of the single crystal of silicon carbide can be enhanced using the methods of the present invention by providing a silicon carbide seed crystal which presents a sublimation surface which is slightly off-axis with respect to one of the Miller index faces. In effect, off-axis silicon carbide crystals tend to transfer three dimensional crystallographic information to the condensing atoms during sublimation. Accordingly, such an off axis growth surface can be used to encourage the repeatable growth of a desired specific silicon carbide polytype. This technique is particularly important when a silicon carbide crystal is being doped with an impurity during sublimation growth. As is known to those familiar with the properties of silicon carbide, particular impurities tend to encourage the growth of specific polytypes of silicon carbide. For example, doping with aluminum is known to favor growth of 4H silicon carbide, but 6H crystals of silicon carbide can be grown with aluminum doping according to the present invention if an off-axis seed is used.

It has further been discovered according to the present invention that the thermal gradient control and indeed the entire process of controlling and maintaining temperatures can be enhanced by using resistance heating, rather than radio frequency (RF) induction heating, in the method of the present invention.

Resistance heating offers a number of advantages in the overall sublimation process. First, resistance heating allows the process to be scaled up to larger crystal diameters than can be handled using induction heating. Induction heating techniques have several limitations which prevent any silicon carbide sublimation processes developed using induction techniques from being similarly scaled up to useful commercial scales. For example, in induction heating, the induction coil must be positioned outside of the vacuum vessel in which the sublimation takes place in order to prevent ionization of the gas (e.g. argon) present in the vessel. Secondly, if the diameter of the sublimation crucibles are increased, the coils used in induction heating tend to heat only the outside layer of the crucible resulting in an undesirable and unacceptable radial thermal gradient. Finally, induction heating requires the use of a glass vacuum vessel to transmit the RF power. As a result, in order to prevent the glass vessel from overheating, either the thermal insulation present must be increased in thickness or the glass must be cooled, typically with water. Increasing the amount of thermal insulation reduces the practical size of the crystal that can be grown, and cooling the vessel with water dramatically reduces the energy efficiency of the entire system.

Alternatively, resistance heating is significantly more energy efficient than induction heating. resistance heating elements can be present within the vacuum vessel. skin heating or radial thermal gradient effects are almost entirely eliminated, and resistance heating permits improved temperature stability and repeatability of processes and control over the entire thermal gradient.

Figures 4 and 5 illustrate some of the apparatus which can be used to accomplish the methods of the present invention. Figure 4 shows a silicon carbide seed crystal 32 upon which a growing crystal 33 has epitaxially attached. The respective crystals 32 and 33 are maintained upon a graphite seed holder 34 which in turn is positioned upon a shaft 35. The remainder of the crucible is defined by graphite walls 36 and a porous graphite barrier 37. The silicon carbide source powder 40 is maintained in a bed 41. In order to ensure a constant supply of silicon carbide powder to a desired position, a rotating shaft 42 which carries a screw lifting mechanism 43 is positioned within a high density graphite cylinder 44. As illustrated in Figure 4, as shaft 42 rotates, the screw mechanism 43 will lift silicon carbide source powder 40 to the top of the screw mechanism to a position adjacent the porous graphite barrier 37. As described earlier, in particular embodiments, the silicon carbide source powder at the top of the high density graphite cylinder 44 is maintained at a temperature of about 2300°C while the temperature of the growth surface of the growing crystal 33 is maintained at a somewhat lower temperature, typically 2200°C.

Moving a continuous supply of silicon carbide source powder to the sublimation region offers several advantages. In particular, and as set forth with respect to the other techniques disclosed herein, the continuous supply further ensures that the subliming source powder generates a consistent flux density. In effect, new source powder is continuously moved into the sublimation area, providing a constant flux as sublimation proceeds.

An optical sight hole 45 is also illustrated, and can be used to either monitor the temperature of the growing crystal

33 using an optical pyrometer or to determine the exact position of the crystal with respect to the silicon carbide source powder 40 at the top of the high density graphite cylinder 44.

In certain embodiments of the invention, the shaft can be pulled in a manner which moves the growth face of the growing crystal 33 away from, or if desired towards, the silicon carbide source powder 40.

5 In yet another embodiment of the invention, the shaft can be rotated to ensure that the temperature profile across the growth face is constant. In such a manner, the crystal can be encouraged to grow symmetrically as the effect of flux variations are damped out and the growing crystal can be prevented from attaching itself to the graphite enclosure.

10 Figure 5 illustrates a number of the same features as Figure 4, but with the separate and independent heating elements illustrated. In Figure 5, the separate and independently controlled resistance heating elements are shown at 46 and 47. As described earlier herein, the upper element 46 can be used to control the temperature of the seed crystal 32 and the growing crystal 33, while the lower heating element 47 can be used to control the temperature of the silicon carbide source powder 40 at the top of the high density graphite cylinder 44. In order to monitor the respective temperatures generated by heating elements 46 and 47, optical sight holes 50 and 51 are provided to permit optical pyrometers to monitor the temperatures generated.

#### EXAMPLE 1

20 A seed was prepared from a 6H alphapolytype silicon carbide. The seed crystal was lapped to insure flatness and then polished with progressively smaller sized diamond paste, finishing with a 0.1 micrometer paste. The seed was cleaned in hot sulfuric acid ( $H_2SO_4$ ) for a period of five minutes, in a one-to-one mixture of ammonium hydroxide ( $NH_4OH$ ) and hydrogen peroxide ( $H_2O_2$ ) for five minutes, in hydrofluoric acid (HF) for one minute, and then finally rinsed in deionized water. The seed was oxidized in dry oxygen at  $1200^\circ C$  for 90 minutes to remove residual polishing damage. The oxide was removed by etching with HF.

25 The seed and source powder were then loaded into the crucible. The source powder consisted of 6H silicon carbide grains having the following size distribution:

	<u>Tyler Mesh Size</u>	<u>Percentage Passing Through</u>	
		<u>(By Weight)</u>	
30	20-40	43	percent
35	40-60	19	percent
	60-100	17	percent
	Over 100	21	percent

40 The loaded crucible was then placed in the sublimation furnace while a slight over pressure of argon was maintained in the furnace to inhibit water contamination, and thus reducing the furnace pump down time. The furnace was evacuated to a base pressure below  $7 \times 10^{-4}$  Pa ( $5 \times 10^{-6}$  Torr). The furnace was heated in a vacuum  $7 \times 10^{-2}$  Pa ( $5 \times 10^{-4}$  Torr) to  $1200^\circ C$  for about ten minutes. It will be understood by those familiar with low pressure systems that an absolute vacuum can never be achieved. Therefore, the term "vacuum" as used herein refers to various systems which are at pressures less than atmospheric pressure, and where appropriate, specific pressures will be employed to best describe the particular conditions. The furnace was then backfilled with argon to a pressure of  $5.3 \times 10^4$  Pa (400 Torr).

45 The temperature of the system was then increased until the top of the crucible was approximately  $2260^\circ C$  and the temperature of the seed is approximately  $2160^\circ C$ , which in the particular system used corresponded to a thermal gradient of  $31^\circ C$  per centimeter (cm). The system was then evacuated slowly over a period of 85 minutes from the pressure of  $5.3 \times 10^4$  Pa (400 Torr) to a pressure of about  $1.3 \times 10^3$  Pa (10 Torr). The system was maintained under these conditions for six hours, after which the system was backfilled with argon to  $1.0 \times 10^5$  Pa (760 Torr) and the temperature reduced to  $200^\circ C$  over a period of 90 minutes.

50 When the furnace was unloaded, the process had resulted in a transparent 6H alpha silicon carbide crystal 12 millimeters (mm) in diameter and 6mm thick.

#### EXAMPLE 2

A 6H Alpha-SiC seed was prepared by cutting the (0001) plane  $3^\circ$  towards the [1120] direction. The seed was then lapped to assure flatness, polished with progressively smaller diamond paste, cleaned, oxidized and etched, all

as described in Example 1.

The source material was doped with aluminum in a quantity of 0.2 weight percent. The seed and source powder were loaded into the crucible, with the source powder having the same powder size distribution as set forth in Example 1. The crucible was loaded, the vessel evacuated, initially heated, and backfilled with argon, all as set forth in Example 1.

The temperature was then increased until the top of the crucible was 2240°C and the seed was 2135°C, corresponding to a thermal gradient of 32°C/cm.

The furnace was evacuated from  $5.3 \times 10^4$  Pa to  $1.3 \times 10^3$  Pa (400 Torr to 10 Torr) as described in Example 1 and the sublimation conditions were maintained for a period of four hours. The furnace was then backfilled with argon to atmospheric pressure ( $1.0 \times 10^5$  Pa) (760 Torr) and the temperature reduced to 200°C over a period of 90 minutes.

When the furnace was unloaded, the process had resulted in a dark blue 6H Alpha-SiC crystal 12mm in diameter and 6mm thick. The resulting crystal was P type and had a carrier concentration of approximately  $10^{18}$  carrier atoms per cubic centimeter.

In the description, preferred and exemplary embodiments of the invention are set forth by way of example and not by way of limitation, the scope of the invention being defined in the following claims.

## Claims

1. A method of reproducibly controlling the growth of large single crystals of a single polytype of silicon carbide independent of the use of impurities as a primary mechanism for controlling polytype growth, and which crystals are suitable for use in producing electrical devices, the method comprising:

introducing a monocrystalline seed crystal (17, 32) of silicon carbide of desired polytype and a silicon carbide source powder (40) into a sublimation system;

raising the temperature of the silicon carbide source powder to a temperature sufficient for the source powder to sublime; while

elevating the temperature of the growth surface of the seed crystal to a temperature approaching the temperature of the source powder but lower than the temperature of the source powder and lower than that at which silicon carbide will sublime under the gas pressure conditions of the sublimation system;

characterized by:

generating and maintaining a constant flow of vaporized Si, Si<sub>2</sub>C, and SiC<sub>2</sub> per unit area per unit time from the source powder (40) to the growth surface of the seed crystal (17, 32) for a time sufficient to produce a desired amount of macroscopic growth of monocrystalline silicon carbide of the desired polytype upon the seed crystal.

2. A method according to claim 1, wherein the step of raising the temperature of the silicon carbide source powder (40) comprises raising the temperature of the silicon carbide source powder to between about 2250° and 2350° centigrade.

3. A method according to claim 1 or 2, wherein the step of elevating the temperature of the seed crystal (17, 32) comprises elevating the temperature of the seed crystal to between about 2150° and 2250° centigrade.

4. A method according to claim 1, 2 or 3, wherein the steps of raising the temperature of the silicon carbide source powder (40) and elevating the temperature of the growth surface of the seed crystal (17, 32) comprise introducing a thermal gradient of 20° centigrade per centimeter between the source powder and the seed crystal.

5. A method according to any preceding claim, wherein the step of introducing a single seed crystal (17, 32) of silicon carbide comprises introducing a seed crystal for which a face corresponding to a low integer Miller index face has been cut to expose a face which is nonperpendicular to an axis normal to the low integer Miller index face which was cut.

6. A method according to any preceding claim, wherein the step of generating and maintaining the substantially constant flow of vaporized Si, Si<sub>2</sub>C, and SiC<sub>2</sub> per unit area per unit time includes introducing a source powder (40) having a selected polytype composition, and maintaining the selected polytype composition in the source powder substantially constant throughout the growth process.

7. A method according to claim 6, wherein the step of maintaining the originally selected composition of polytypes in the source powder comprises replenishing the source powder during the sublimation process using source powder

replenishment having a polytype composition which will maintain the originally selected polytype composition in the source powder substantially constant in the sublimation system.

- 5 8. A method according to any preceding claim, wherein the step of generating and maintaining the substantially constant flow of vaporized Si, Si<sub>2</sub>C, and SiC<sub>2</sub> per unit area per unit time includes introducing a source powder (40) having a selected predetermined distribution of surface areas, and maintaining the selected distribution of surface areas in the source powder substantially constant throughout the growth process.
- 10 9. A method according to claim 8, wherein the step of maintaining the originally selected predetermined distribution of surface areas comprises replenishing the source powder (40) during the sublimation processing using source powder replenishment having a distribution of surface areas which will maintain the originally selected distribution of surface areas substantially constant in the source powder in the sublimation system.
- 15 10. A method according to any preceding claim, wherein the step of generating and maintaining the substantially constant flow of vaporized Si, Si<sub>2</sub>C, and SiC<sub>2</sub> per unit area per unit time includes introducing a source powder (40) having a selected predetermined distribution of particle sizes, and maintaining the selected distribution of particle sizes in the source powder substantially constant throughout the growth process.
- 20 11. A method according to claim 10, wherein the step of maintaining the originally selected predetermined distribution of particle sizes comprises replenishing the source powder (40) during the sublimation process using source powder replenishment having a distribution of particle sizes which will maintain the originally selected distribution of particle sizes substantially constant in the source powder in the sublimation system.
- 25 12. A method according to claim 9 or 10, wherein the step of replenishing the source powder (40) during the sublimation process using source powder having a selected distribution of particle sizes comprises introducing silicon carbide powder having the following size distribution as determined by the weight percentage of a sample which will pass through a designated Tyler mesh screen:

Tyler Mesh Screen	Weight Percentage Passed
20-40	43%
40-60	19%
60-100	17%
Over 100	21%

- 30 35 40 45 50 55 13. A method according to any preceding claim, wherein the step of generating and maintaining the substantially constant flow of vaporized Si, Si<sub>2</sub>C, and SiC<sub>2</sub> per unit area per unit time from the source powder (40) to the growth surface of the seed crystal (17, 32) includes increasing the thermal gradient between the seed crystal and the source powder as the crystal grows and the source powder is used up, to thereby maintain an absolute temperature difference between the source powder and seed crystal which continues to be most favorable for crystal growth and to continuously encourage further crystal growth beyond that which would be obtained by maintaining a constant thermal gradient.
- 14. A method according to claim 13, wherein the step of increasing the thermal gradient between the seed crystal (17, 32) and the source powder (40) comprises increasing the temperature of the source powder, while maintaining the temperature of the growth surface of the seed crystal at the initial temperature lower than that of the source powder.
- 15. A method according to claim 13 or 14, wherein the step of increasing the thermal gradient comprises increasing the thermal gradient from about 20° centigrade per centimeter to about 50° centigrade per centimeter.
- 16. A method according to any of claims 1 to 12, wherein the step of generating and maintaining the substantially constant flow of vaporized Si, Si<sub>2</sub>C, and SiC<sub>2</sub> per unit area per unit time from the source powder (40) to the growth surface of the seed crystal (17, 32) includes maintaining a constant thermal gradient as measured between the growth surface of the seed crystal and the source powder as the crystal grows and the source powder is used up, while maintaining the growth surface of the seed crystal and the source powder at their respective different temperatures, to thereby maintain a constant growth rate of the single seed crystal and a consistent growth of a single

polytype upon the single growth surface of the seed crystal.

5 17. A method according to claim 16, wherein the step of maintaining the constant thermal gradient between the growth surface of the seed crystal (17, 32) and the source powder (40) comprises providing relative movement between the growth surface of the seed crystal and the source powder as the seed crystal grows, while maintaining the source powder at the temperature sufficient for silicon carbide to sublime and the seed crystal at the temperature approaching the temperature of the source powder but lower than the temperature of the source powder and lower than that at which silicon carbide will sublime.

10 18. A method according to claim 16, wherein the step of maintaining the constant thermal gradient between the growth surface of the seed crystal and the source powder comprises maintaining a fixed distance between the growth surface of the seed crystal and the source powder as the crystal grows.

15 19. A method according to claim 16, wherein the step of maintaining the constant thermal gradient between the growth surface of the seed crystal and the source powder comprises independently controlling the source powder and seed crystal temperatures by separately monitoring the temperature of the source powder and the temperature of the seed crystal and separately adjusting the temperature of the source powder and the temperature of the seed crystal.

20 20. A method according to any preceding claim, including the step of rotating the seed crystal (17, 32) as the seed crystal grows and as the source powder (40) is used up to thereby maintain a constant temperature profile across the growth surface of the seed crystal, to dampen the effect of flux variations, and to prevent the growing crystal (33) from becoming attached to undesired mechanical portions of the sublimation system.

25 21. A method according to any of claims 1 to 12, wherein the step of generating and maintaining a substantially constant flow of vaporized Si, Si<sub>2</sub>C, and SiC<sub>2</sub> per unit area per unit time from the source powder to the growth surface of the seed crystal includes introducing a thermal gradient between the source powder (40) and the seed crystal (17, 32) and then increasing the thermal gradient between the seed crystal and the source powder as the crystal grows and the source powder is used up, to thereby maintain an absolute temperature difference between the source powder and seed crystal which continues to be most favorable for crystal growth and to continuously encourage further crystal growth beyond that which would be obtained by maintaining a constant temperature gradient.

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#### Patentansprüche

35 1. Verfahren zur reproduzierbaren Steuerung des Wachstums großer Einkristalle eines einzigen Polytypus von Siliziumcarbid unabhängig von der Verwendung der Dotierungsstoffe als ein primärer Mechanismus zur Steuerung des Polytypenwachstums, so daß diese Kristalle zur Verwendung bei der Herstellung elektrischer Geräte geeignet sind, wobei das Verfahren umfaßt:

40 Einführung eines monokristallinen Impfkristalls (17, 31) aus Siliziumcarbid des gewünschten Polytyps und eines Siliziumcarbid-Vorratspulvers (40) in ein Sublimationssystem:  
Erhöhen der Temperatur des Siliziumcarbid-Vorratspulvers auf eine ausreichende Temperatur, bei der das Vorratspulver sublimiert; während

45 die Temperatur der Wachstumsoberfläche des Impfkristalls auf eine Temperatur angehoben wird, die sich der Temperatur des Vorratspulvers nähert, aber niedriger ist als die Temperatur des Vorratspulvers und niedriger als die Temperatur, bei der das Siliziumcarbid unter den Gasdruckbedingungen des Sublimationssystems sublimieren wird:

50 gekennzeichnet durch:  
Erzeugung und Aufrechterhaltung eines konstanten Durchsatzes verdampften Si, Si<sub>2</sub>C und SiC<sub>2</sub> pro Flächeneinheit pro Zeiteinheit von dem Vorratspulver (40) zur Wachstumsoberfläche des Impfkristalls (17, 32) über eine ausreichende Zeit, um auf dem Impfkristall den gewünschten Betrag an makroskopischem Wachstum von monokristallinem Siliziumcarbid des gewünschten Polytyps zu erzeugen.

55 2. Verfahren gemäß Anspruch 1, bei dem der Schritt der Anhebung der Temperatur des Siliziumcarbid-Vorratspulvers (40) das Anheben der Temperatur des Siliziumcarbid-vorratspulvers auf zwischen ca. 2250° und 2350° Celsius umfaßt.

3. Verfahren gemäß Anspruch 1 oder 2, bei der der Schritt der Anhebung der Temperatur des Impfkristalls (17, 32) die Erhöhung der Temperatur des Impfkristalls auf zwischen ca. 2150° und 2250° Celsius umfaßt.

5 4. Verfahren gemäß Anspruch 1, 2 oder 3, bei dem die Schritte der Anhebung der Temperatur des Siliziumcarbid-vorratspulvers (40) und der Anhebung der Temperatur der Wachstumsoberfläche des Impfkristalls (17, 32) die Einführung eines Wärmegradienten von 20° Celsius pro Zentimeter zwischen dem Vorratspulver und dem Impfkristall umfassen.

10 5. Verfahren gemäß einem der vorstehenden Ansprüche, bei dem der Schritt der Einführung eines einzelnen Impfkristalls (17, 32) aus Siliziumcarbid die Einführung eines Impfkristalls umfaßt, für das eine Fläche entsprechend einer kleinen ganzzahligen Miller-Index-Fläche herausgeschnitten worden ist, um eine Fläche freizulegen, die nicht senkrecht steht zu einer Achse, die senkrecht zu der herausgeschnittenen Miller-Index-Fläche steht.

15 6. Verfahren gemäß einem der vorstehenden Ansprüche, bei dem der Schritt der Erzeugung und Aufrechterhaltung des im wesentlichen konstanten Durchsatzes verdampften Si, Si<sub>2</sub>C und SiC<sub>2</sub> pro Flächeneinheit pro Zeiteinheit die Einführung eines Vorratspulvers (40) mit einer gewählten Polytypenzusammensetzung und die im wesentlichen konstante Aufrechterhaltung der gewählten Polytypenzusammensetzung in dem Vorratspulver über den gesamten Wachstumsprozeß beinhaltet.

20 7. Verfahren gemäß Anspruch 6, bei dem der Schritt der Aufrechterhaltung der ursprünglich gewählten Zusammensetzung von Polytypen in dem Vorratspulver das Nachfüllen des Vorratspulvers während des Sublimationsprozesses unter Verwendung einer VorratspulverNachfüllung mit einer Polytypenzusammensetzung umfaßt, die die ursprünglich gewählte Polytypenzusammensetzung in dem Vorratspulver in dem SublimationsSystem im wesentlichen konstant hält.

25 8. Verfahren gemäß einem der vorstehenden Ansprüche, bei dem der Schritt der Erzeugung und Aufrechterhaltung des im wesentlichen konstanten Durchsatzes verdampften Si, Si<sub>2</sub>C und SiC<sub>2</sub> pro Flächeneinheit pro Zeiteinheit die Einführung eines Vorratspulvers (40) mit einer gewählten vorgegebenen Verteilung von Oberflächenbereichen enthält und die gewählte Verteilung von Oberflächenbereichen in dem Vorratspulver über den gesamten Wachstumsprozeß im wesentlichen konstant gehalten wird.

30 9. Verfahren gemäß Anspruch 8, bei dem der Schritt der Aufrechterhaltung der ursprünglich gewählten vorgegebenen Verteilung von Oberflächenbereichen das Nachfüllen des Vorratspulvers (40) während der Sublimationsbehandlung unter Verwendung einer Vorratspulver-Nachfüllung mit einer Verteilung von Oberflächenbereichen umfaßt, die die ursprünglich gewählte Verteilung von Oberflächenbereichen in dem Vorratspulver in dem Sublimationssystem im wesentlichen konstant hält.

35 10. Verfahren gemäß einem der vorstehenden Ansprüche, bei dem der Schritt der Erzeugung und Aufrechterhaltung des im wesentlichen konstanten Durchsatzes verdampften Si, Si<sub>2</sub>C und SiC<sub>2</sub> pro Flächeneinheit pro Zeiteinheit die Einführung eines Vorratspulvers (40) mit einer gewählten vorgegebenen Verteilung von Partikelgrößen und die im wesentlichen konstante Aufrechterhaltung der gewählten Verteilung der Partikelgrößen in den Vorratspulver über den gesamten Wachstumsprozeß beinhaltet.

40 11. Verfahren gemäß Anspruch 10, bei dem der Schritt der Aufrechterhaltung der ursprünglich gewählten vorgegebenen Verteilung der Partikelgrößen das Nachfüllen des Vorratspulvers (40) während des Sublimationsprozesses unter Verwendung einer Vorratspulver-Nachfüllung mit einer Verteilung von Partikelgrößen umfaßt, die die ursprünglich gewählte Verteilung der Partikelgrößen in dem Vorratspulver in dem Sublimations-system im wesentlichen konstant hält.

45 12. Verfahren gemäß Anspruch 9 oder 10, bei dem der Schritt der Nachfüllung des Vorratspulvers (40) während des Sublimationsprozesses unter Verwendung von Vorratspulver mit einer gewählten Verteilung von Partikelgrößen die Einführung von Siliziumcarbid-pulver mit der folgenden Größenverteilung umfaßt, die anhand des prozentualen Gewichtsanteils einer Probe bestimmt wird, der ein spezielles Tyler-Sieb passiert:

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Maschenweite Tyler-Sieb	Passierter Prozentsatz
20 - 40	43%
40 - 60	19%

(fortgesetzt)

Maschenweite Tyler-Sieb	Passierter Prozentsatz
60 - 100	17%
über 100	21%

5 13. Verfahren gemäß einem der vorstehenden Ansprüche, bei dem der Schritt der Erzeugung und Aufrechterhaltung des im wesentlichen konstanten Durchsatzes von verdampftem Si, Si<sub>2</sub>C und SiC<sub>2</sub> pro Flächeneinheit pro Zeiteinheit aus dem Vorratspulver (40) zu der Wachstumssoberfläche des Impfkristalls (17, 32) die Erhöhung des Wärmegradienten zwischen dem Impfkristall und dem Vorratspulver mit wachsendem Kristall und sich verbrauchendem Vorratspulver enthält, um dadurch eine absolute Temperaturdifferenz zwischen dem Vorratspulver und dem Impfkristall aufrechtzuerhalten, die für das Kristallwachstum weiterhin am günstigsten ist, und um kontinuierlich ein weiteres Kristallwachstum über dasjenige hinaus zu fördern, das man durch einen konstanten Wärmegradienten erhalten würde.

10 14. Verfahren gemäß Anspruch 13, bei dem der Schritt der Erhöhung des Temperaturgradienten zwischen dem Impfkristall (17, 32) und dem Vorratspulver (40) die Erhöhung der Temperatur des Vorratspulvers umfaßt, während die Temperatur der Wachstumssoberfläche des Impfkristalls auf der Anfangstemperatur gehalten wird, die niedriger ist als diejenige des Vorratspulvers.

15 15. Verfahren gemäß Anspruch 13 oder 14, bei dem der Schritt der Erhöhung des Temperaturgradienten die Erhöhung des Temperaturgradienten von etwa 20° Celsius pro Zentimeter auf etwa 50° Celsius pro Zentimeter umfaßt.

20 16. Verfahren gemäß einem der Ansprüche 1 bis 12, bei dem der Schritt der Erzeugung und Aufrechterhaltung des im wesentlichen konstanten Durchsatzes von verdampftem Si, Si<sub>2</sub>C und SiC<sub>2</sub> pro Flächeneinheit pro Zeiteinheit aus dem Vorratspulver (40) zur Wachstumssoberfläche des Impfkristalls (17, 32) die Aufrechterhaltung eines konstanten Wärmegradienten, gemessen zwischen der Wachstumssoberfläche des Impfkristalls und dem Vorratspulver, beinhaltet, während der Kristall anwächst und das Vorratspulver aufgebraucht wird, wobei die Wachstumssoberfläche des Impfkristalls und das Vorratspulver auf ihren jeweiligen verschiedenen Temperaturen gehalten werden, um dadurch eine konstante Wachstumsrate des einzelnen Impfkristalls und ein konstantes Wachstum eines einzelnen Polytypen auf der einzelnen Wachstumssoberfläche des Impfkristalls aufrechtzuerhalten.

25 17. Verfahren gemäß Anspruch 16, bei dem der Schritt der Aufrechterhaltung des konstanten Wärmegradienten zwischen der Wachstumssoberfläche des Impfkristalls (17, 32) und dem Vorratspulver (40) die Bereitstellung einer relativen Bewegung zwischen der Wachstumssoberfläche des Impfkristalls und dem Vorratspulver mit anwachsendem Impfkristall umfaßt, während das Vorratspulver auf der Temperatur gehalten wird, die für eine Sublimierung des Siliziumcarbids ausreichend ist, und der Impfkristall auf einer sich der Temperatur des Vorratspulvers annähernden, jedoch niedrigeren Temperatur und einer niedrigeren Temperatur gehalten wird als diejenige, bei der das Siliziumcarbid sublimieren wird.

30 18. Verfahren gemäß Anspruch 16, bei dem der Schritt der Aufrechterhaltung des konstanten Temperaturgradienten zwischen der Wachstumssoberfläche des Impfkristalls und dem Vorratspulver die Aufrechterhaltung eines festen Abstands zwischen der Wachstumssoberfläche des Impfkristalls und dem Vorratspulver bei anwachsendem Kristall umfaßt.

35 19. Verfahren gemäß Anspruch 16, bei dem der Schritt der Aufrechterhaltung des konstanten Temperaturgradienten zwischen der Wachstumssoberfläche des Impfkristalls und dem Vorratspulver die unabhängige Steuerung der Temperaturen des Vorratspulvers und des Impfkristalls umfaßt, indem die Temperatur des Vorratspulvers und des Impfkristalls getrennt überwacht und indem die Temperatur des Vorratspulvers und des Impfkristalls getrennt eingestellt werden.

40 20. Verfahren gemäß einem der vorstehenden Ansprüche, enthaltend den Schritt der Drehung des Impfkristalls (17, 32) mit anwachsendem Impfkristall und sich aufbrauchendem Vorratspulver (40), um dadurch ein konstantes Temperaturprofil über die Wachstumssoberfläche des Impfkristalls aufrechtzuerhalten, um den Effekt der Flußschwankungen zu dämpfen und um zu verhindern, daß ein anwachsender Kristall (33) in unerwünschter Weise an mechanischen Abschnitten des Sublimations-systems anhaftet.

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21. Verfahren gemäß einem der Ansprüche 1 bis 12, bei dem der Schritt der Erzeugung und Aufrechterhaltung des im wesentlichen konstanten Durchsatzes von verdampftem Si, Si<sub>2</sub>C und SiC<sub>2</sub> pro Flächeneinheit pro Zeiteinheit aus dem Vorratspulver zur Wachstums Oberfläche des Impfkristalls die Einführung eines Wärmegradienten zwischen dem Vorratspulver (40) und dem Impfkristall (17, 32) und dann die Erhöhung des Wärmegradienten zwischen den Impfkristall und dem Vorratspulver mit anwachsendem Kristall und sich aufbrauchendem Vorratspulver beinhaltet, um dadurch eine absolute Temperaturdifferenz zwischen dem Vorratspulver und dem Impfkristall aufrechtzuerhalten, die weiterhin für das Wachstum am günstigsten ist, und um das weitere Kristallwachstum um dasjenige hinaus zu fördern, das man durch Aufrechterhaltung eines konstanten Temperaturgradienten erhalten würde.

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#### Revendications

15. 1. Procédé pour conduire de façon reproductible la croissance de grands monocristaux d'un unique polytype de carbure de silicium, indépendant de l'utilisation d'impuretés en tant que mécanisme primaire pour conduire la croissance du polytype, et lesquels cristaux conviennent pour être utilisés dans la production de dispositifs électriques, le procédé consistant à :

20. introduire un cristal germe monocristalin (17, 32) de carbure de silicium du polytype désiré et une poudre source de carbure de silicium (40) dans un système de sublimation ;  
 éllever la température de la poudre source de carbure de silicium à une température suffisante pour que la poudre source se sublimé ; et, en même temps  
 éllever la température de la surface de croissance du cristal germe jusqu'à une température approchant la température de la poudre source mais inférieure à la température de la poudre source et inférieure à celle à 25. laquelle le carbure de silicium se sublimé dans les conditions de pression gazeuse du système de sublimation :

caractérisé par une phase consistant à :

30. engendrer et entretenir un débit constant de SiC, Si<sub>2</sub>C et SiC<sub>2</sub> vaporisés par unité de surface et par unité de temps s'écoulant de la poudre source (40) à la surface de croissance du cristal germe (17, 32) pendant un temps suffisant pour produire une quantité désirée de croissance macroscopique de carbure de silicium monocristalin du polytype désiré sur le cristal germe.

35. 2. Procédé selon la revendication 1, dans lequel la phase consistant à éllever la température de la poudre source de carbure de silicium (40) consiste à éllever la température de la poudre source de carbure de silicium jusqu'à entre environ 2250° et 2350° centigrades.

40. 3. Procédé selon la revendication 1 ou 2, dans lequel la phase consistant à éllever la température du cristal germe (17, 32) consiste à éllever la température du cristal germe jusqu'à entre environ 2150° et 2250° centigrades.

45. 4. Procédé selon la revendication 1, 2 ou 3, dans lequel les phases consistant à éllever la température de la poudre source de carbure de silicium (40) et à éllever la température de la surface de croissance du cristal germe (17, 32) consiste à introduire un gradient thermique de 20° centigrades par centimètre entre la poudre source et le cristal germe.

50. 5. Procédé selon une quelconque des revendications précédentes, dans lequel la phase consistant à introduire un unique cristal germe (17, 32) de carbure de silicium consiste à introduire un cristal germe pour lequel une face correspondant à une face d'indice de Miller petit et entier a été taillée pour mettre à nu une face qui est non perpendiculaire à un axe normal à la face d'indice de Miller petit et entier qui a été taillée.

55. 6. Procédé selon une quelconque des revendications précédentes, dans lequel la phase consistant à engendrer et entretenir le débit sensiblement constant de SiC, Si<sub>2</sub>C et SiC<sub>2</sub> vaporisés par unité de surface et par unité de temps consiste à introduire une poudre source (40) ayant une composition de polytypes choisie, et à maintenir la composition de polytypes choisie dans la poudre source sensiblement constante pendant tout le processus de croissance.

7. Procédé selon la revendication 6, dans lequel la phase consistant à maintenir la composition de polytypes initialement choisie dans la poudre source consiste à compléter la poudre source pendant le processus de sublimation en utilisant un complément de poudre source ayant une composition de polytypes qui maintiendra la composition

de polytypes initialement choisie dans la poudre source sensiblement constante dans le système de sublimation.

5 8. Procédé selon une quelconque des revendications précédentes, dans lequel la phase consistant à engendrer et à entretenir le débit sensiblement constant de SiC, Si<sub>2</sub>C et SiC<sub>2</sub> vaporisés par unité de surface et par unité de temps consiste à introduire une poudre source (40) ayant une distribution pré-déterminée choisie de surfaces spécifiques et à maintenir la distribution choisie de surfaces spécifiques dans la poudre source sensiblement constante pendant tout le processus de croissance.

10 9. Procédé selon la revendication 8, dans lequel la phase consistant à maintenir la composition de polytypes initialement choisie dans la poudre source consiste à compléter la poudre source (40) pendant le processus de sublimation en utilisant un complément de poudre source ayant une distribution de surfaces spécifiques qui maintiendra la distribution de surfaces spécifiques initialement choisie sensiblement constante dans la poudre source dans le système de sublimation.

15 10. Procédé selon une quelconque des revendications précédentes, dans lequel la phase consistant à engendrer et à entretenir le débit sensiblement constant de SiC, Si<sub>2</sub>C et SiC<sub>2</sub> vaporisés par unité de surface et par unité de temps consiste à introduire une poudre source (40) ayant une distribution pré-déterminée choisie de dimensions de particules et à maintenir la distribution choisie de dimensions de particules dans la poudre source sensiblement constante pendant tout le processus de croissance.

20 11. Procédé selon la revendication 10, dans lequel la phase consistant à entretenir la composition de polytypes initialement choisie dans la poudre source consiste à compléter la poudre source (40) pendant le processus de sublimation en utilisant un complément de poudre source ayant une distribution de dimensions de particules qui maintiendra la distribution de dimensions de particules initialement choisie sensiblement constante dans la poudre source dans le système de sublimation.

25 12. Procédé selon la revendication 9 ou 10, dans lequel la phase de complémentement de la poudre source (40) pendant le processus de sublimation en utilisant une poudre source ayant une distribution choisie de dimensions de particules consiste à introduire de la poudre de carbure de silicium ayant la distribution de dimensions suivante, déterminée par le pourcentage en poids d'un échantillon qui passe au tamis Tyler indiqué :

Tamis Tyler	Pourcentage en poids passant
20 - 40	43%
40 - 60	19%
60 - 100	17%
plus de 100	21%

35 13. Procédé selon une quelconque des revendications précédentes, dans lequel la phase consistant à engendrer et entretenir le débit sensiblement constant de SiC, Si<sub>2</sub>C et SiC<sub>2</sub> vaporisés par unité de surface et par unité de temps s'écoulant de la poudre source (40) à la surface de croissance du cristal germe (17, 32) comprend la phase consistant à augmenter le gradient thermique entre le cristal germe et la poudre source au fur et à mesure que le cristal croît et que la poudre source s'épuise, pour maintenir de cette façon une différence de température absolue entre la poudre source et le cristal germe qui continue à être la plus favorable pour la croissance cristalline et à favoriser ainsi continuellement la poursuite de la croissance cristalline au-delà de celle qu'on aurait obtenue en maintenant un gradient thermique constant.

40 14. Procédé selon la revendication 13, dans lequel la phase consistant à augmenter le gradient thermique entre le cristal germe (17, 32) et la poudre source (40) consiste à augmenter la température de la poudre source tout en maintenant la température de la surface de croissance du cristal germe à la température initiale inférieure à celle de la poudre source.

45 15. Procédé selon la revendication 13 ou 14, dans lequel la phase consistant à augmenter le gradient thermique consiste à porter le gradient thermique d'environ 20° centigrades par centimètre à environ 50° centigrades par centimètre.

50 16. Procédé selon une quelconque des revendications 1 à 12, dans lequel la phase consistant à engendrer et entretenir

le débit sensiblement constant de SiC, Si<sub>2</sub>C et SiC<sub>2</sub> vaporisés par unité de surface et par unité de temps s'écoulant de la poudre source (40) à la surface de croissance du cristal germe (17, 32) comprend la phase consistant à maintenir un gradient thermique constant, mesuré entre la surface de croissance du cristal germe et la poudre source pendant que le cristal croît et que la poudre source s'épuise, tout en maintenant la surface de croissance du cristal germe et la poudre source à leurs différentes températures respectives, pour maintenir de cette façon un taux de croissance constant de l'unique cristal germe et une croissance stable d'un polytype unique sur l'unique surface de croissance du cristal germe.

5 17. Procédé selon la revendication 15, dans lequel la phase consistant à maintenir le gradient thermique constant entre la surface de croissance du cristal germe (17, 32) et la poudre source (40) comprend la phase consistant à établir un mouvement relatif entre la surface de croissance du cristal germe et la poudre source pendant que le cristal germe croît, tout en maintenant la poudre source à la température suffisante pour que le carbure de silicium se sublime et le cristal germe à la température qui s'approche de la température de la poudre source mais est inférieure à la température de la poudre source et inférieure à celle à laquelle le carbure de silicium se sublime.

10 18. Procédé selon la revendication 16, dans lequel la phase consistant à maintenir le gradient thermique constant entre la surface de croissance du cristal germe et la poudre source consiste à maintenir une distance fixe entre la surface de croissance du cristal germe et la poudre source lorsque le cristal croît.

15 19. Procédé selon la revendication 16, dans lequel la phase consistant à maintenir le gradient thermique constant entre la surface de croissance du cristal germe et la poudre source consiste à régler indépendamment les températures de la poudre source et du cristal germe en contrôlant séparément la température de la poudre source et la température du cristal germe et en ajustant séparément la température de la poudre source et la température du cristal germe.

20 25 20. Procédé selon une quelconque des revendications précédentes comprenant la phase consistant à faire tourner le cristal germe (17, 32) pendant que le cristal germe croît et que la poudre source (40) s'épuise, pour maintenir ainsi un profil de température constant d'un bord à l'autre de la surface de croissance du cristal germe, afin d'atténuer l'effet des variations du débit et d'éviter que le cristal (33) en cours de croissance n'adhère à des parties mécaniques indésirables du système de sublimation.

30 35 21. Procédé selon une quelconque des revendications 1 à 12, dans lequel la phase consistant à engendrer et entretenir un débit sensiblement constant de SiC, Si<sub>2</sub>C et SiC<sub>2</sub> vaporisés par unité de surface et par unité de temps s'écoulant de la poudre source à la surface de croissance du cristal germe comprend la phase consistant à introduire un gradient thermique entre la poudre source (40) et le cristal germe (17, 32), puis à augmenter le gradient thermique entre le cristal germe et la poudre source au fur et à mesure que le cristal croît et que la poudre source s'épuise, pour maintenir de cette façon une différence de température absolue entre la poudre source et le cristal germe qui continue à être la plus favorable pour la croissance du cristal et à favoriser continuellement la poursuite de la croissance du cristal au-delà de celle qu'on aurait obtenue en maintenant un gradient de température constant.

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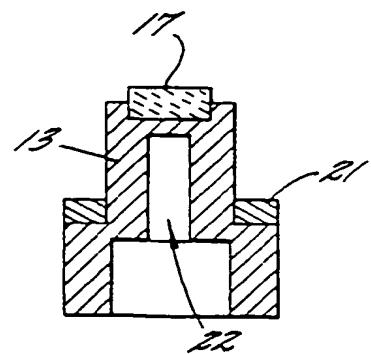
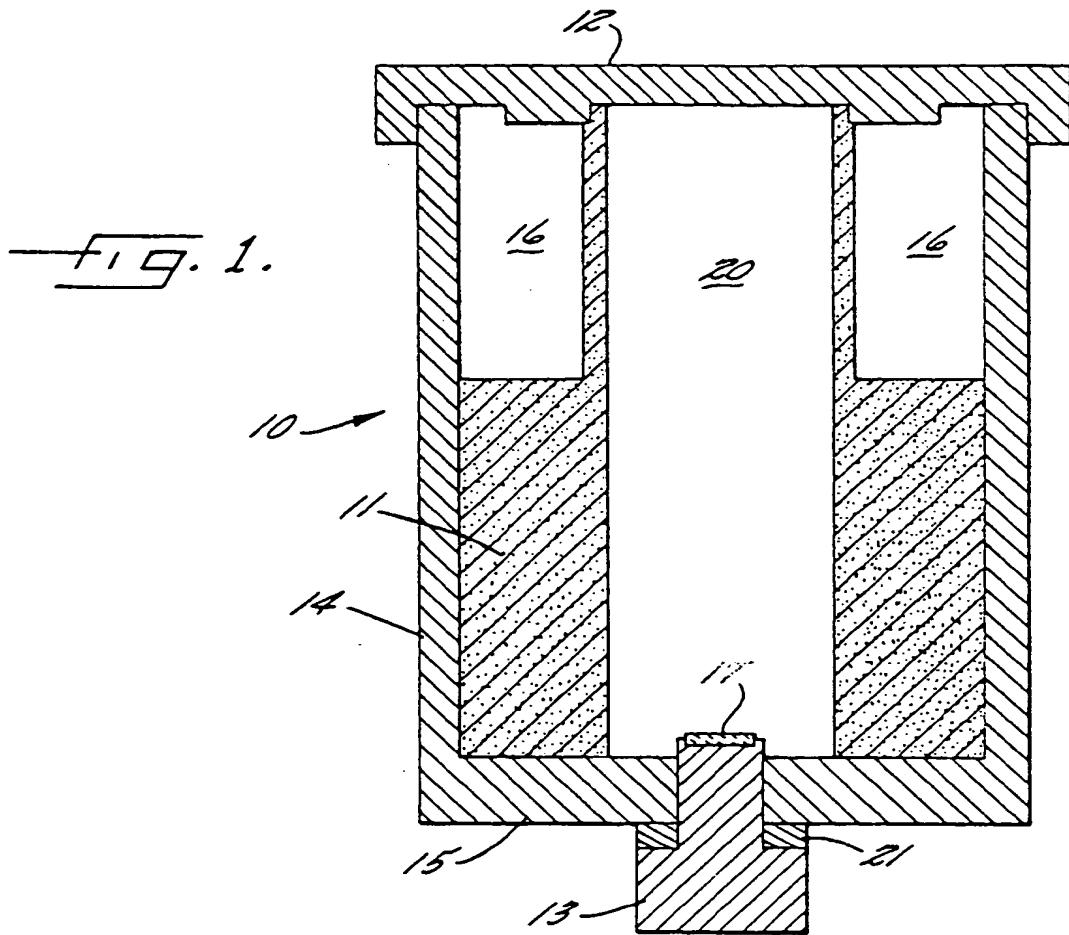
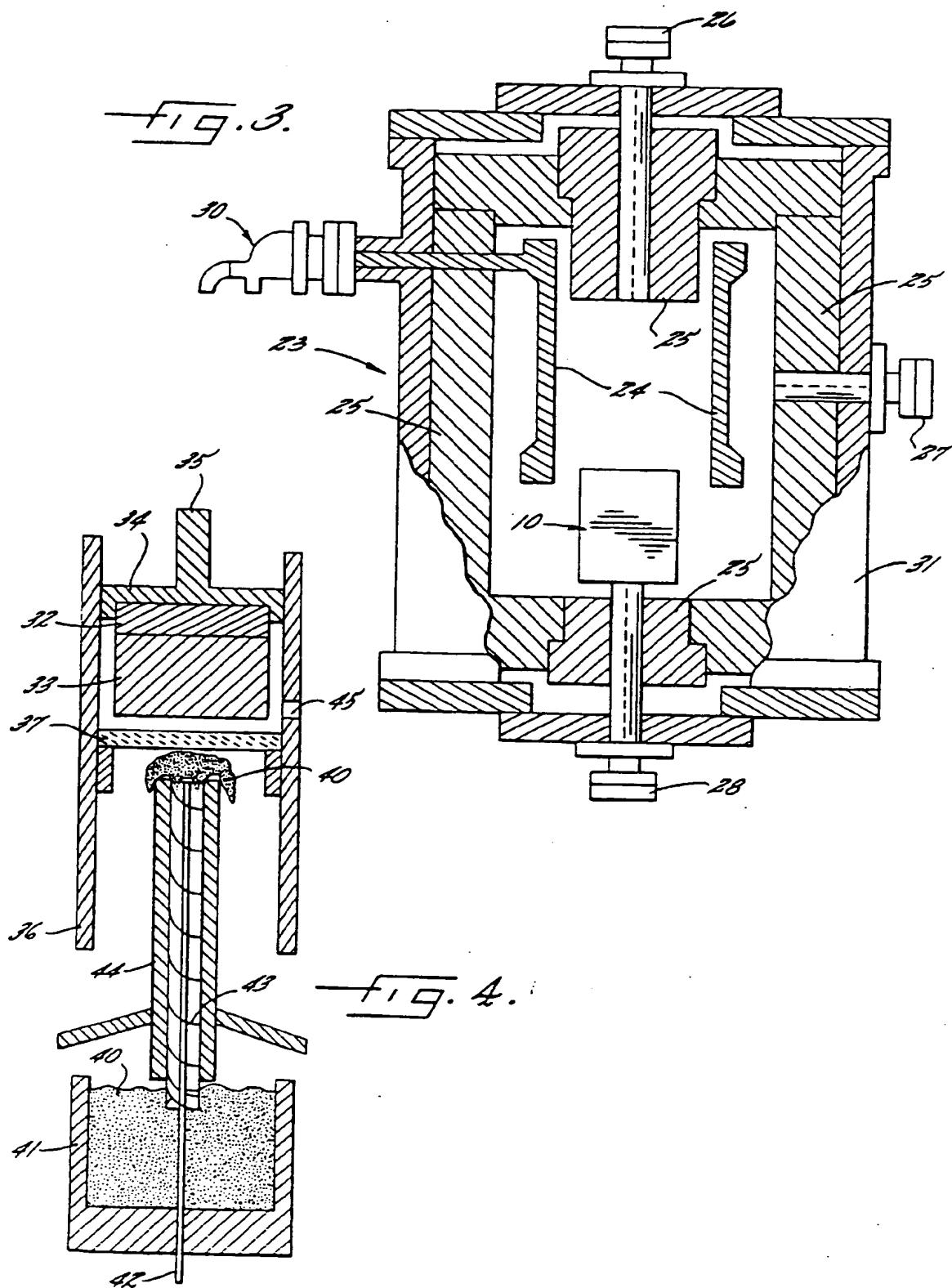
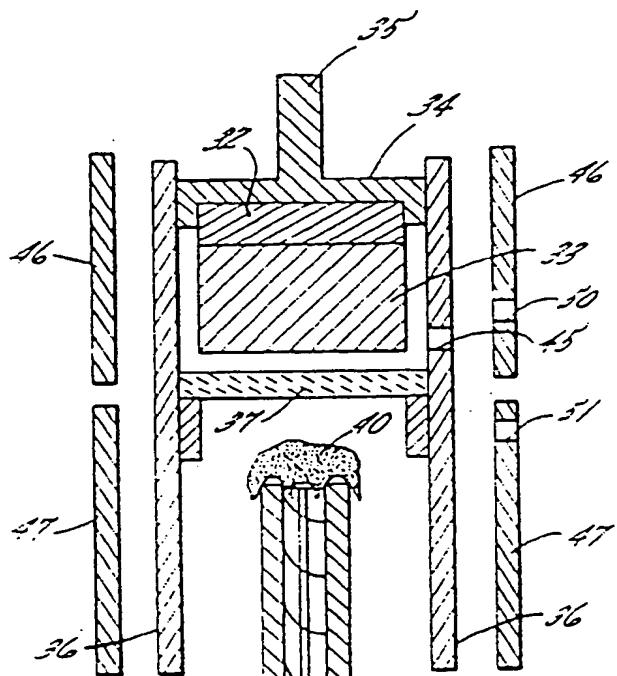
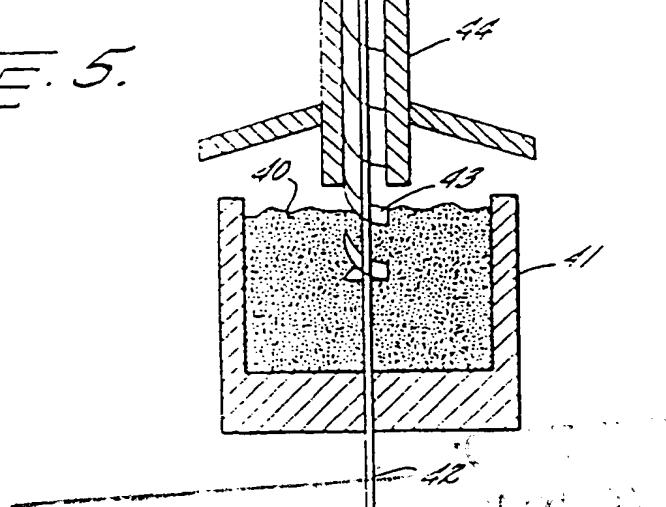


FIG. 2.





—FIG. 5.



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